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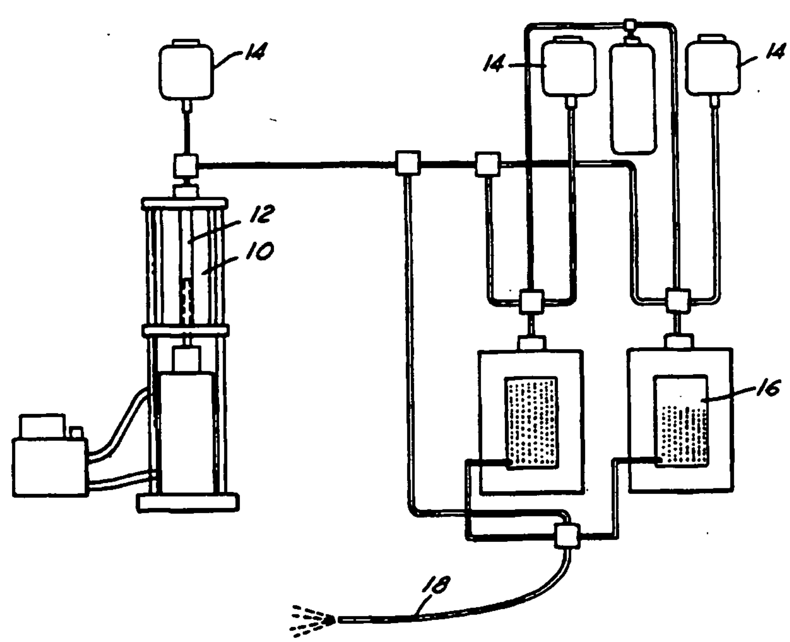

(57) Abstract

A method of injecting gas-supersaturated fluid (14) as a bubble-free effluent (18) from a delivery system into a relatively low pressure, gas-depleted environment without cavitation or bubble formation. The method includes the steps of eliminating (12) cavitation nuclei from within the delivery system, compressing (16) a liquid and a gas at a high partial pressure to form a gas-supersaturated liquid, and ejecting (18) the gas-supersaturated liquid through the delivery system into the environment without associated cavitation formation in the effluent.

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METHOD FOR DELIVERING A GAS-SUPERSATURATED FLUID TO A GAS-DEPLETED SITE AND USE THEREOF

Technical Field

This invention relates to a method for delivering a gas-supersaturated fluid from a high pressure environment to a gas-depleted site at a lower pressure without the immediate onset of cavitation or bubbling.

Background Art

The maximum concentration of gas achievable in a liquid ordinarily is governed by Henry's Law. At ambient pressure, the relatively low solubility of many gases, such as oxygen or nitrogen, within a liquid such as water produces a low concentration of the gas in the liquid. However, there are many applications wherein it would be advantageous to employ a gas concentration within the liquid which greatly exceeds its solubility at ambient pressure. Compression of a gas/liquid mixture at a high pressure can be used to achieve a high dissolved gas concentration, but disturbance of a gas-supersaturated liquid by attempts to eject it into a 1 bar environment from a high pressure reservoir ordinarily results in cavitation inception at or near the exit port. The rapid evolution of bubbles produced at the exit port vents much of the gas from the liquid, so that a high degree of gas-supersaturation no longer exists in the liquid at ambient pressure, outside the high pressure vessel. In addition, the presence of bubbles in the effluent impedes the flow of the effluent beyond the exit port.

In my co-ending application Serial No. 152,589, filed November 15, 1993, I described a method for stabilization of a stream of oxygen-supersaturated water which permitted ejection of the stream from a high pressure vessel into a 1 bar environment without cavitation inception in the effluent at or near the exit port(s). An effluent of water containing oxygen at a concentration on the order of 4 cc oxygen/g of injectate, representing a partial pressure of approximately 140 bar of the dissolved gas, can be ejected from a high pressure vessel into a 1 bar liquid environment with complete absence of cavitation inception in the ejected stream. In air at 1 bar, cavitation inception is delayed until breakup of the ejected stream into droplets.

The complete absence of cavitation inception in water supersaturated with oxygen at a high concentration permits its in vivo infusion into either venous or arterial blood for the purpose of increasing the oxygen concentration of blood without incurring the formation of bubbles which would otherwise occlude capillaries.

In addition to this application as previously described, a wide variety of other applications would benefit from ejection of a gas-supersaturated liquid from a high pressure reservoir to ambient pressure in a manner which is unassociated with cavitation inception at or near the exit port. For example, organic material and plant waste streams, e.g., paper mills and chemical plants, often require an increase in dissolved oxygen content before the discharge of such waste streams in a body of water. U.S. Patent No. 4,965,022 also recognizes that a similar need may also occur at municipal waste

treatment plants. Also noted therein is that fish farms require increased dissolved oxygen levels to satisfy the needs of high density aquaculture. Other applications are disclosed in my U.S. Patent No. 5,261,875.

U.S. Patent No. 4,664,680 discloses enriching the oxygen content of water. That reference discloses that a number of conventional apparatus types can be used for continuously contacting liquid and oxygen-containing gas streams to effect oxygen absorption. To avoid premature liberation of dissolved oxygen before it is incorporated within the bulk of matter to be enriched in oxygen content, pressurizable confined flow passageways are used.

Other oxygen saturation devices are disclosed in U.S. Patent Nos. 4,874,509; and 4,973,558. These and other approaches leave unsolved the need to infuse gas enriched fluid solutions from a high pressure reservoir toward a reaction site at a lower pressure without cavitation or bubble formation in the effluent at or near the exit port.

Summary of the Invention

A method is described for ejection of gas-supersaturated liquids from a high pressure reservoir to a relatively low pressure environment, including ambient pressure, which permits the use of the gas-supersaturated liquid at the lower pressure without immediate cavitation inception. Cavitation nuclei in the liquid are removed by compression in a high pressure reservoir. The use of suitable channels at the distal end of the system for delivery of the gas-supersaturated liquid,

along with elimination of cavitation nuclei along the inner surface of the channels, allows ejection of the liquid into a relatively low pressure environment without cavitation inception at or near the exit port.

Thus, an important aspect of the invention described herein is the use of small capillary channels at the distal end of the delivery system, along with initial hydrostatic compression of liquid in the range of 0.5 to 1.0 kbar to remove cavitation nuclei along the inner surface of the channels. Cavitation nuclei and bubbles in the liquid are removed in the high pressure reservoir by either hydrostatic compression or compression from a source of gas maintained at a pressure which would provide the desired concentration of gas in the liquid. Hydrostatic compression to 0.5 to 1.0 kbar rapidly removes cavitation nuclei and bubbles in the liquid, but much lower pressures from a gas source are as effective, although requiring longer periods of time. When a gas source is used to both pressurize the liquid and achieve a desired gas concentration in the liquid, the range of gas pressure would typically be in the 10 bar to 150 bar range.

As a result of the lack of cavitation inception at or near the exit port, a stream of gas-supersaturated liquid can be used to enrich a gas-deprived liquid with gas outside the high pressure reservoir simply by convection of the gas-supersaturated effluent with the gas-deprived liquid at ambient pressure. Enrichment of a gas-deprived liquid with gas by diffusion from the gas phase to the liquid is, by contrast, an extremely slow process. The lack of bubbles in the effluent additionally permits unimpeded ejection into

the gas-deprived liquid. When the gas-supersaturated liquid is ejected in an air environment, the lack of cavitation inception at or near the exit port permits the use of the effluent in a manner similar to the same liquid which is not supersaturated with gas, i.e., the ejected stream remains intact until breakup into droplets as would ordinarily occur, rather than disintegration into a diffuse spray near the exit port from rapid growth of gas nuclei.

Detailed Description of the Preferred Embodiment and Best Modes For Carrying Out The Invention

I now describe a modification of my earlier work, along with representative examples of practical applications of the method.

In order to initiate flow of oxygen-supersaturated water through capillary channels, such as silica tubings, it had been necessary to use an internal diameter at the exit port on the order of 10 microns or less. However, it has been discovered that flow of gas-supersaturated water can resume or continue through the larger proximal portion of the capillary tubing, once cavitation nuclei have been eliminated from a channel along its entire length. Elimination may be achieved, for example, by application of hydrostatic pressure.

As the internal diameter of the tubing increases, the maximum oxygen concentration which can be perfused through its length into a 1 bar aqueous medium without cavitation inception is reduced. For example, the maximum oxygen concentration which can be used in this manner for a 100 micron internal diameter silica

tubing is approximately 1.5 cc oxygen/g, while that for a 25 micron tubing is approximately 3 cc oxygen/g. Thus, larger bore capillary tubings can be used to deliver an effluent free of bubble formation, once cavitation nuclei are eliminated.

Accordingly, there has been discovered an inverse relationship between the tubing internal diameter and the maximum oxygen concentration allowable. Channels as large as 1 mm or greater can probably be used, but the maximum oxygen concentration which could be achieved without bubble production in the effluent would be less than that for the 100 micron tubing.

Experimental Procedure

A double-ended, high pressure vessel (Leco, Tem-Press Div.) having a honed cylindrical cavity with a 30 cc capacity was filled with 5 g % dextrose in water, equilibrated with oxygen at 800 psi. The oxygen-supersaturated fluid was transferred at 800 psi from a 300 cc capacity Parr bomb after equilibration overnight. The Leco vessel was isolated from the Parr bomb, and a piston, positioned at the proximal end of the Leco vessel and sealed with O-rings, was driven against the oxygen-supersaturated fluid at approximately 0.7 kbar hydrostatic pressure from a hydraulic compressor.

The fluid was delivered through, for example, a 100 micron internal diameter/363 micron outer diameter fused silica tubing (Polymicro Technologies) which had been tapered to 7 microns with a propane torch. After several minutes of hydrostatic compression to remove cavitation nuclei and determination that no bubbles appeared in the effluent as confirmed by use of argon-

ion laser illumination of fluorescein dye in the fluid, the silica tubing was cleaved several millimeters proximal to the tapered section. The internal diameter at the distal end of the tubing then was 100 microns.

No cavitation inception occurred over a period of many hours, including refilling of the Leco vessel from the Parr bomb on multiple occasions. Even when the pressure in the Leco vessel was allowed to fall to 1 bar, no bubbles in the effluent, containing 1.3 to 2.0 cc oxygen/g, were noted. When a second 100 micron silica tubing containing cavitation nuclei was placed in parallel with the first tubing, a prominent stream of bubbles was ejected from the second tubing, and no bubbles were noted in the first tubing. However, after use of a tapered distal end and transient hydrostatic pressure to 0.7 kbar, no bubbles were noted in the second tubing after cleavage of the tapered tip so that the internal diameter at the distal end was 100 microns.

In a preferred system, a hydraulic compressor is used to apply 0.5 to 1.0 kbar liquid water pressure to eliminate cavitation nuclei on the inner surface of channels, such as those fabricated from multibore silica tubing, at the distal end of the delivery system. The liquid can either be either gas-depleted or gas enriched. Elimination of cavitation nuclei in the bulk gas-supersaturated liquid can be achieved simply by compression with gas at the desired partial pressure of the gas. Thus, when initiating flow through the silica tubing, high pressure liquid from the hydraulic compressor is used first, and subsequent flow of gas-supersaturated liquid would be delivered from a reservoir under pressure from gas tank.

When O2 gas compresses water before it is supersaturated, the combination of the gas pressure dissolving cavitation nuclei in the water and sufficient standing without excessive agitation (freestanding bubbles are inherently unstable-either they grow and rise to the surface or dissolve, although cavitation nuclei on the surfaces of the container or associated with motes may not disappear) eliminates bubbles. Therefore, when gas-supersaturated water flows from the vessel pressurized from the O2 tank, no bubbles in the effluent are noted. If an occasional bubble or a cavitation nucleus associated with a crevice in a mote flows through the tubing at the distal end of the delivery system, the stability of the effluent is unaffected. Very likely, when a bubble in the bulk liquid passes through the tubing, a thing film of liquid separates the bubble from the surface of the tubing, thereby inhibiting the formation of a cavitation nucleus. By contrast, if cavitation nuclei are present on the inner surface of the tubing, they generate rapid growth of bubbles continuously in the effluent.

The advantages inherent in the use of an O2 gas source as the driving pressure for delivery of the O2-supersaturated fluid include the fact that only one hydraulic compressor is needed to "prepare" the catheter for use. The hydraulic compressor would very likely then no longer be needed. The volume of flow can be adjusted by simply using the appropriate number of channels for a given i.d. The gas source would simultaneously provide the partial pressure required to achieve a desired concentration of gas in the water and the driving pressure for delivery of the gas-supersaturated water through the channels at the distal end of the

delivery system. The gas pressure used for this dual purpose would be on the order of 150 to 2000 psi.

Alternatively, a hydraulic compressor is used to drive gas-supersaturated liquid through channels at the distal end of the delivery system. In order to maintain a relatively constant pressure, either two reciprocating hydraulic compressors would be used or a sufficiently large reservoir would be interposed between the compressor and the channels, such that the pressure drop in the reservoir occurring during refilling of a single compressor is not excessive.

A simple approach to achieve a high hydrostatic pressure, on the order of 0.5 to 1.0 kbar, within capillary channels to eliminate cavitation nuclei is to taper the distal end to a small diameter, on the order of < 20 microns, prior to application of the pressure. Alternatively, relatively gas-depleted liquid can be perfused through larger channels at the same driving pressure; although a pressure drop at the distal end of the channels reduces the degree of hydrostatic compression at this location, the relative lack of gas in the liquid helps to dissolve cavitation nuclei at the lower pressure. The gas-supersaturated water at 1.5 to 2.0 cc oxygen/g can then be delivered through the non-tapered distal end into water without cavitation inception. Once cavitation nuclei are eliminated, flow of oxygen supersaturated water through the 100 micron tubing into water can be achieved without bubble formation in the effluent. The pressure in the high pressure vessel can then be lowered to 1 bar for many hours. With the distal end of the tubing stored in ordinary tap water overnight, flow of an oxygen-supersaturated water, after

transient compression to 0.5 to 1 kbar, can be resumed without cavitation inception in the free stream.

Other ways may be used to eliminate cavitation nuclei throughout the length of the tubing. Temporarily capping the distal end of the channels to allow full hydrostatic pressure to be applied to the end of the channels prior to ejection (after removing the cap) is effective.

Alternatively,.a scavenger of the gas may be deployed in the liquid within the tubing, prior to flow of the gas-supersaturated liquid. Examples of the latter approach for removing oxygen-containing gas nuclei along the surface of the channels include a sodium sulfite solution or a solution of deoxyhemoglobin. Either substance would bind oxygen and remove the gas nuclei.

Electrochemical reduction of oxygen in gas nuclei within, for example, a metal tubing may be used at the distal end of the system for delivery of oxygen-supersaturated water to eliminate the nuclei.

Although application of a strong vacuum or heating the liquid within the tubing to a high temperature might be used to remove cavitation nuclei along the inner surface of the channels, hydrostatic compression of the liquid (particularly a degassed one if necessary) is preferable.

There are several advantages in the use of channels having an internal diameter larger than 10 microns: a much fewer number of channels are necessary

to deliver an equivalent flow; adequate filtration of the gas-supersaturated liquid to prevent occlusion of the channels is much simpler to achieve; and the flow rate and velocity can be adjusted more easily by use of channels or tubings having a suitable length.

For example, a 30 micron internal diameter fused silica tubing (Polymicro Technology), approximately 3 feet in length, will result in a flow velocity of approximately 200 cm/sec and a flow rate of approximately 0.09 cc/min, when oxygen-supersaturated 5 g% dextrose in water (approximately 3. cc oxygen/g) is pressurized to 0.7 kbar and delivered through the tubing into blood at physiologic pressure. Higher flow velocities may result in hemolysis, so that use of the appropriate length of the tubing is helpful in adjustment of the velocity to an appropriately low level. By use of a bundle of 30 micron internal diameter tubings, along with adjustment of the driving pressure between 1 bar to 1 kbar, after initial hydrostatic compression to 0.5 to 1 kbar, the overall flow rate can be varied to provide the desired rate of oxygen delivery.

While silica or glass capillary tubing is disclosed, channels may also be defined within quartz, a metal, hollow carbon fibers, a ceramic, sapphire, or diamond.

As described in my copending application Serial No. 152,589, filed November 15, 1993, delivery of an oxygen-supersaturated physiologic solution into a vein or a right heart chamber can be used for either partial or complete support of systemic oxygenation of patients. Intra-arterial delivery of the fluid can be

used to achieve blood oxygen tensions much higher than that achievable by breathing oxygen to improve local oxygen delivery to hypoxic or ischemic tissues.

For example, I have been able to oxygenate blood in vitro in the following manner. Venous blood was exposed to nitrogen to lower the oxygen tension to very low levels, on the order of < 20 mm Hg. Aliquot parts of 20 cc were placed in a plastic beaker and covered with Parafilm. One section of the wall of the beaker was replaced with a thin plastic film, so that an ultrasonic transducer could be positioned against the film, with an ultrasonic gel used as a coupling agent. A two dimensional image of the volume of blood was continuously monitored. An electrode (Diamond General, Ann Arbor) was placed within the blood for continuous monitoring of the partial pressure of oxygen.

One or more silica capillary tubings, having channel(s) ranging from 5 microns to 100 microns in internal diameter were used to deliver oxygen-supersaturated, cavitation nucleus-free 5 g% dextrose in water from a high pressure vessel (Leco) into the blood. The threshold partial pressure of oxygen at which multiple bubbles appeared by ultrasound was recorded. A mean partial pressure of oxygen of 800 to 900 mm Hg was achieved before the onset of bubble formation in approximately 20 runs.

Thus, the oxygen tensions achievable in blood are higher than 1 bar. Considering that, in a hyperbaric oxygen chamber, air is compressed rather than pure oxygen, the partial pressure of oxygen achievable in such chambers pressurized to 2-3 bar are on the order of

only 350 to 650 mm Hg. In addition, the high oxygen tensions in the compressed gas result in lung toxicity upon exposure for more than a few hours. Infusion of oxygen-supersaturated physiologic solutions into arterial blood, in contrast to the use of a hyperbaric chamber, can be used to achieve higher oxygen tension levels and do so for a much longer period of time. Treatment of local tissue hypoxia or ischemia by this approach can be achieved by placement of a catheter within the arterial blood supply of the target tissue.

Table A discloses examples of and derivations from experimental observations made during the practice of the present invention. When an O_L gas source is used to provide the driving pressure, at 10 to 150 bar, the minimum length is reduced by a factor equal to the ratio of 0.7 kbar to the gas pressure.

Table A

EXAMPLES DERIVED FROM EXPERIMENTAL OBSERVATIONS

Internal Diameter Of Silica Tubing	Max. Flow/Tube	Min. Length	Max. Oxygen	No. of Tubes	Flow Rate	Diameter of Bundle
Microns	cc/min	cm	cc/g		g/min.	mm
100	0.94	1006	1.5	35	33.0	0.84
50	0.24	252	2.2	95	23.0	0.69
25	0.059	63	3.0	282	17.0	0.59
15	0.021	22.6	3.3	722	15.0	0.57
10	0.0094	10.1	3.6	1478	14.0	0.54
6	0.0034	3.6	4.0	3676	12.5	0.51
5	0.0024	2.5	4.1	5081	12.2	0.50
4	0.0015	1.6	4.2	7937	11.9	0.50
3	0.00085	0.91	4.4	13369	11.4	0.49
2	0.00038	0.4	4.8	27412	10.4	0.47
1	0.000094	0.1	5.0	106383	10.0	0.46
0.5	0.000024	0.025	5.2	400641	9.6	
0.25	0.0000059	0.0063	5.4	1569366	9.3	

The number of tubes describes the capillary array at the distal end of the catheter. The maximum oxygen delivery at 0.7 kbar equaled 50 cc's of oxygen per minute for each diameter. The minimum length is based on a maximum flow velocity of 200 centimeters per second. Though higher velocities are possible, prolonged use of higher velocities may result in hemolysis of red cells.

Other Uses

A. ***MRI***

Since oxygen is paramagnetic, infusion of oxygen-supersaturated solutions into blood would be expected to enhance imaging of blood and oxygenated tissues by magnetic resonance imaging (MRI). That is, an oxygen-supersaturated solution would be expected to act as an MRI contrast agent.

B. ***Topical Applications***

If oxygen-supersaturated physiologic solution or water were placed in contact with a body surface, including skin and wounds, a marked increase in the rate of diffusion of oxygen into tissue would occur, since the partial pressure of the gas could be made to be as high as approximately 140 bar.

In addition, as water diffuses across a body surface, oxygen in the gas-supersaturated fluid would be transported, thereby enhancing the rate of diffusion of the gas into tissue.

In wounds which are ischemic, the improved oxygen levels in tissue would increase the rate of healing. For a large surface area to mass ratio, such as in young infants or neonates, contact of most of the surface area of the body (excluding the head) with oxygen-supersaturated fluid may result in a significant increase in blood oxygen tension levels, when oxygenation by ventilation alone is associated with systemic hypoxemia.

Ventilation with oxygen-supersaturated physiologic solutions could be used to support systemic oxygenation in patients with respiratory insufficiency. Inflation of atelectatic regions of the lung with oxygen-supersaturated liquids would be more effective than air or O2 gas in expanding alveoli and more effective in enhancing oxygen diffusion to pulmonary capillaries. In addition, inflation of the lung with the liquid would simultaneously be useful to remove unwanted lung exudates.

Topical application of oxygen-supersaturated solutions to wounds, in addition to relieving tissue hypoxia, could be used to clean, debride, and sterilize such tissues. Hydrogen peroxide solutions are used currently for these purposes, but cells within granulation tissue may be damaged along with bacteria by peroxide solutions. In contrast, a hyperbaric oxygen solution would be toxic to bacteria and beneficial to tissue within the wound.

C. Industrial Applications

The ability to inject a gas-supersaturated fluid into a relatively low pressure environment without immediate cavitation inception would find utility in many industrial applications. The following applications are representative examples.

1. Fire Extinguishing. When cavitation-free, gas-supersaturated water is ejected at a high velocity from the distal end of a tube, gas nucleation occurs after breakup of the stream into droplets because of the inherent tensile strength of water. If an inert gas, such as nitrogen, carbon dioxide, or argon is dissolved

in water at a supersaturated concentration and compressed to remove cavitation nuclei, a stream of water containing the gas under high pressure can be delivered into a 1 bar air or liquid environment without cavitation taking place near the exit port.

For example, nitrogen can be dissolved at a pressure of approximately 150 bar in water either before or after 0.5 to 1.0 kbar hydrostatic compression to remove cavitation nuclei. The stream of water that can be ejected from a suitable tubing preserves the metastability of the fluid by the absence of cavitation nuclei. Upon contact of the gas-supersaturated stream of water with solid surfaces, spontaneous breakup into droplets occurs and the gas is released suddenly. A similar result follows heating.

To extinguish a fire, the gas release will be beneficial in at least 3 ways. The expansion of the gas will aid the dispersion of water over a broader volume; expansion of gas results in cooling; and the inert gas will displace oxygen in the air. Although this method of extinguishing a fire would be expected to be more costly, it should make more efficient use of water and, more importantly, it should be more effective than the conventional use of water. Such benefits are enhanced in draught-stricken areas and in other situations where there is difficulty in delivering enough extinguishing water to the incendiary area.

I conducted a test of this application in the following manner. A jet stream of water, delivered from a high pressure vessel at 0.7 kbar and having a velocity of approximately 2,000 cm/sec through a 10 micron i.d.

silica tubing, was directed at the flame of a laboratory propane torch. The flow rate of propane was adjusted so that the apex of the inner blue portion of the flame coincided with the end of the metal collar. Starting with a distance of about 8 inches between the distal end of the silica tubing and the apex of the blue portion of the flame, the distance was reduced until the flame was either extinguished or the distance was less than 1 inch.

With no gas in the water, a mean distance of 2 to 3 inches was required in 3 runs to extinguish the flame. In one run, the flame could not be extinguished. In another, a distance of approximately 1 inch was required.

In contrast, when water was supersaturated with argon at 1700 psi (approximately 3 cc gas/g) and hydrostatically compressed to 0.8 kbar to eliminate cavitation nuclei, a mean distance of approximately 4.5 to 5 inches was effective in abolishing the flame in each of 4 runs. The silica tip and flow conditions for these runs were identical to those without gas in the water.

Thus, it is clear that the use of water supersaturated with an inert gas, stabilized by hydrostatic compression and use of the tapered silica tip, was far more effective than the use of water alone for extinguishing the flame of the propane torch.

2. ***Purification and Carbonation of Beverages***. Water used for human consumption undergoes multiple steps to ensure purity and lack of contaminants which could affect

either health or taste. One commonly used initial step is chemical treatment to oxidize contaminants.

Infusion of oxygen-supersaturated, cavitation-free water is a more efficient method of oxidation than the use of oxygen gas (since oxygenation of water by convection is more efficient that by diffusion), and would be nontoxic, in contrast to the use of peroxides.

Once water for the beverage has been purified, carbon dioxide is usually introduced prior to sealing it in a bottle or can (or an undercover gasser may be used for cans). The gas is usually introduced under high pressure at a low temperature in order to increase its dissolved concentration. The use of water supersaturated with carbon dioxide and treated to remove all cavitation nuclei would allow the process of carbonation to be conducted at virtually any ambient room temperature, thereby obviating the need for cooling. If the inside walls of the containers were also free of significant cavitation nuclei, it should be possible to store the beverage at room temperature and to open the container at the higher than usual temperature without prominent bubble evolution and without significant loss of the carbonation.

An interesting alternative to the use of carbon dioxide to provide effervescence in beverages is the use of oxygen, air, or nitrogen. The limited solubility of these gases ordinarily precludes their use for this purpose. However, by mixing water supersaturated with any of the gases with a syrup concentrate immediately before consumption, a gas yield of the

resultant beverage would be similar to that currently used in carbonated beverages.

When oxygen or air is used in this manner, the hyperbaric oxygen content in the beverage would help maintain sterility, and its consumption would be expected to have a more favorable inhibitory effect on bacterial pathogens in the oral cavity compared to the use of carbon dioxide.

3. __Steelmaking__. During the process of making steel, an oxygen "lance" is used to deliver oxygen gas initially to the surface of the crude metal melt and subsequently to deeper layers with the help of cooling water jets adjacent to the high velocity oxygen. The purpose of the oxygen treatment is to oxidize undesirable materials such as carbon and silicon. The frothy mixture which is produced floats at the top of the melt and is poured off, leaving the purified molten steel.

The use of water supersaturated with oxygen would be expected to be more effective in penetrating the molten metal compared to the stream of oxygen gas. The oxidation process would therefore be more rapid and complete, resulting in a steel having superior yield characteristics and a more efficient method.

4. __Delignification Of Wood Pulp__. Bleaching of wood pulp and its delignification require oxygen which is introduced either as a gas or in the form of hydrogen peroxide. The use of oxygen supersaturated water would be a far more efficient means of oxygenation of the slurry containing the wood pulp, and higher levels of

oxygen tension could be obtained compared to the use of oxygen gas.

Following such treatment, the effluent would be less toxic compared to the use of hydrogen peroxide. In addition, the latter would be expected to be more expensive than the use of oxygen-supersaturated water.

5. __Wastewater/Bioreactor Treatment__. All currently available methods of treatment of wastewater are based on some means of mixing air or oxygen gas with water and rely on the slow process of diffusion from the gas to the liquid phase for oxygenation of the wastewater. Similarly, most methods for introducing oxygen into bioreactors, which are used to produce a byproduct such as a drug, rely on mixing oxygen gas with water within which organisms are suspended. The rate of oxygen consumption by some organisms is quite rapid, so that introducing oxygen sufficiently rapidly has inspired the design of many types of bioreactors.

The basic mass transfer steps (i.e. the steps through which oxygen must pass) in moving from air (or oxygen-enriched air) to the reaction site in a biological species consist of: transport through the gas film inside the bubble; across the bubble-liquid interface; through the liquid film around the bubble; across the well-mixed bulk liquid (broth); through the liquid film around the biological species; and finally transport within the species (e.g. cell, seed, microbial species) to the bio-reaction site. Each step offers a resistance to oxygen transfer. The rate-limiting step typically occurs at the air-liquid interface.

The use of oxygen supersaturated water would be far more rapid than currently available methods, since (as noted earlier) oxygenation by convection is significantly more rapid than by diffusion, and would allow fine control of the optimal partial pressure of oxygen within the bioreactor.

In the biotechnology field, the supply of oxygen to a growing biological species (aeration) in an aerobic bio-reactor is one of the most critical requirements in biotechnology. Aeration is usually accomplished by transferring oxygen from the air into the fluid surrounding the biological species from whence it is, in turn, transferred to the biological species itself. The rate at which oxygen is demanded by the biological species in a bio-reactor depends on the species, its concentration, and on the concentration of other nutrients in the surrounding fluid.

The main reason for the importance of aeration lies in the limited solubility of oxygen and water, a value which decreases in the presence of electrolytes and other solutes as temperature increases. A typical value for the solubility of oxygen (the equilibrium saturation concentration) and water in the presence of air at atmospheric pressure at 25°C is about 0.008 g of oxygen per m^3 (i.e. about 8 ppm).

In addition to each bio-reaction demanding oxygen at a different rate, there is a unique relationship for each between the rate of reaction and the level of dissolved oxygen.

6. ***Oxygenation of Ponds, ...kes, Streams, Aquariums, Fisheries, Swimming Pools and Municipal Drinking Water***. In order to promote an aerobic environment in these bodies of water, oxygen within air is mixed within the water. As noted above, this process is inefficient because of the relatively slow process of diffusion from the gas phase into the liquid.

Injection of air- or oxygen-supersaturated water into such bodies of water would not only be a far more efficient means of transfer of oxygen, but a high velocity stream of the gas-supersaturated water would penetrate far more effectively into large bodies of water than either a gas or a gas/water mixture. The stream could be directed from a more superficial location to penetrate deep layers of water, in contrast to the need to position a gas/water mixing apparatus or a bubble generator within deep layers of water.

7. ***Cleaning Of Surfaces***. Water jets are commonly employed to c- an surfaces of ctory floors, the exterior of bu ings, b idges, ga e.g., air).

Super turated water woul be expected to e more efficient, since the sudden expansion of the g upon contact with the surface would provide an additional force for removal of surface materials. Cavitation inception upon contact with the surface would act in a similar manner to the action of sandblasting, but would not, in contrast, pose an environmental concern.

8. ***Enhancement Of Chemical Reactions***. When a chemical reaction involves the use of a gas in a liquid medium, the rate of reaction at ambient pressure will be

enhanced by the use of a gas-supersaturated liquid. In addition, in exothermic reactions, wherein it is desirable to avoid an excessive rise in temperature, the liquid carrying the gas at a supersaturated concentration could be used as ballast.

Injection of water supersaturated with either oxygen or air into or onto an organic fuel for enhancement of combustion and control of temperature represents one such example. Similarly, if liquid fuel is supersaturated with air or oxygen and cavitation nuclei have been removed within the delivery system containing the gas-supersaturated fuel, combustion of the fuel upon its ejection from the high pressure vessel and upon ignition would be expected to proceed more rapidly than the use of the fuel alone. The high pressure of oxygen within the fuel, along with a broad surface area presented when the stream of fuel breaks up into droplets and subsequently microscopic bubbles, would be responsible for the improved rate of combustion.

9. __Snowmaking__. With the use of conventional snowmaking equipment, e.g., for recreational skiing, the ice particles are produced before ejection into the atmosphere. Therefore, the distance which the snow can be blown with air is limited. When air-supersaturated water is ejected at a high velocity into ambient air, cavitation nuclei are formed after breakup of the stream into a fine mist. During expansion of gas, nuclei form during or after breakup of the stream into a mist, and the temperature of each droplet will fall as a result of expansion of the gas.

Strobe light photography at a 20 ns exposure (Xenon Corp.) under a light microscope has demonstrated that each droplet of gas-supersaturated water is transformed into a bubble. If the temperature of the water is near 0°C at the time of ejection from a high pressure reservoir, the fall in temperature will convert each droplet into a particle of ice or snow.

Use of water at high pressure has the additional advantage of depressing its freezing point. For example, at 1 kbar, the freezing point of water is approximately -11°C. Thus, the water could be ejected at a temperature even below 0°C, and gas expansion would cool the resultant ice particles to a yet lower temperature. Ejection of a stream of water, supersaturated with air, into the atmosphere could be used to cover much greater distances than that achievable with conventional snowmaking equipment. Fewer machines would be required with this method to cover the same area with artificial snow, which would be a more efficient and, very likely, more economical means of snowmaking.

10. __Other Uses.__ The physical and chemical properties of a liquid supersaturated with a gas differ from either that of the liquid or the gas. Such properties are too numerous to elaborate, but include, in alphabetical order, the boiling point, chemical potential, compressibility, density, dielectric constant, enthalpy, free energy, heat capacity, magnetic susceptibility, specific heat, surface tension, thermal conductivity, and viscosity.

The ability to use a liquid supersaturated with a gas at a relatively low pressure is the basis of

all applications of the invention. Accordingly, use of any physical or chemical property of gas-supersaturated liquids at a relatively low pressure falls within the scope of the invention.

What Is Claimed Is:

1. A method of injecting gas-supersaturated fluids as a bubble-free effluent from a delivery system into a gas-depleted environment, comprising the steps of:

a. eliminating cavitation nuclei from within the delivery system;

b. compressing a liquid and a gas to form a gas-supersaturated liquid; and

c. ejecting the gas-supersaturated liquid through the delivery system into the environment without associated cavitation formation in the effluent at or near the exit position.

2. The method of claim 1 wherein the nuclei in the delivery system are removed by hydrostatic compression with a liquid having a relatively low concentration of the nuclei.

3. The method of claim 1 wherein the nuclei in the delivery system are removed by hydrostatic compression with the gas-supersaturated effluent.

4. The method of claim 1 wherein the nuclei in the delivery system are removed by perfusion with a solution containing a scavenger of the nuclei.

5. The method of claim 1 wherein the nuclei in the delivery system are removed electrochemically.

6. The method of claim 1 wherein the nuclei in the delivery system are removed by capping the distal

end of the delivery system and applying hydrostatic pressure.

7. The method of claim 1 wherein the nuclei in the delivery system are removed by applying a vacuum during immersion of the delivery system in a liquid.

8. The method of claim 1 wherein the gas is dissolved in the fluid at a high partial pressure of the gas prior to compression of the fluid.

9. The method of claim 1 wherein the fluid is hydrostatically compressed prior to exposure to a high partial pressure of the gas.

10. The method of claim 1 wherein aliquot parts of the gas and the fluid are hydrostatically compressed together.

11. The method of claim 1 wherein the hydrostatic pressure is varied over a 10 bar to 10 kbar range after transient application of a 0.3 to 1.0 kbar pressure.

12. The method of claim 1 wherein the delivery system includes channels each having an internal diameter in a range of 0.1 micron to 10 cm.

13. The method of claim 1 wherein the fluid is water.

14. The method of claim 1 wherein the gas is oxygen.

15. The method of claim 1 wherein the gas is an inert gas.

16. The method of claim 1 wherein the gas is air.

17. The method of claim 1 wherein the gas is carbon dioxide.

18. The method of claim 13 or 14 wherein the environment is blood.

19. The method of claims 13 or 14 or 16 wherein the environment is a bioreactor.

20. The method of claims 13 or 14 or 16 wherein the environment is wastewater.

21. The method of claims 13 or 14 or 16 wherein the environment is potable water.

22. The method of claims 13 or 14 or 16 wherein the environment is a fishery.

23. The method of claims 13 or 14 or 16 wherein the environment is a lake, pond, stream, swimming pool, or municipal water.

24. The method of claims 13 or 14 or 16 wherein the environment is a slurry of wood pulp.

25. The method of claims 13 or 14 or 16 wherein the environment is molten metal.

26. The method of claims 13 or 15 wherein the environment is a fire and materials undergoing combustion.

27. The method of claim 1 wherein the environment is within a chemical reactor.

28. The method of claims 13 or 16 wherein ejection of air-supersaturated water into ambient air at a temperature near 0°C produces ice or snow.

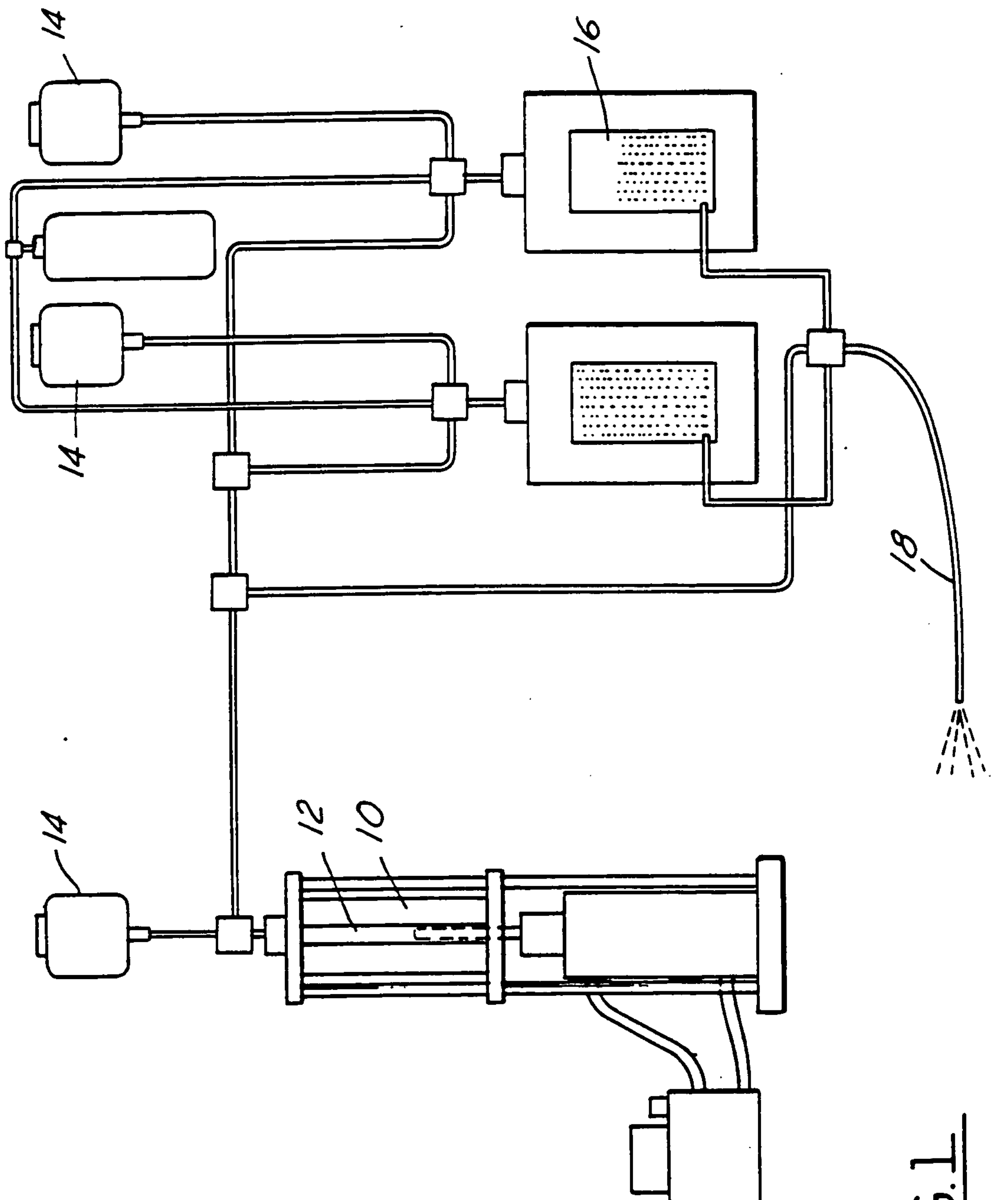

FIG.1

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/07991

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :A61B 19/00; A61M 1/14, 1/34, 37/00;
US CL :128/898; 422/44; 604/24
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 128/898; 422/44; 604/24

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APD, DIALOG

Search Terms: cavitation nuclei, supersaturation, bubble free

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,973,558 (WILSON ET AL.) 27 November 1990, see entire document.	23-28
A	US, A, 5,209,720 (UNGER) 11 May 1993, see entire document.	1-28
A	US, A, 5,215,680 (D'ARRIGO) 01 June 1993, see entire document.	1-28
Y, P	US, A, 5,407,426 (SPEARS) 18 April 1995, see entire document, and claims 1-27.	1-22
A	US, A, 4,644,808 (LECOFFRE) 24 February 1987, see references to cavitation nuclei.	1-28
A	US, A, 4,372,491 (FISHGAL) 08 February 1983, see references to cavitation nuclei.	1-28

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be part of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
09 AUGUST 1995	05 SEP 1995

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,645,518 (ROFFELSEN) 24 February 1987, see references to cavitation nuclei.	1-28
A	US, A, 4,874,509 (BULLOCK) 17 October 1989, see entire document.	1-28
A	US, A, 4,664,680 (WEBER) 12 May 1987, see entire document.	1-28